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PROGRESS REPORT

OFFICE OF NAVAL RESEARCH
Contract Nonr-1129(00)
Project NR 036-012

Period Covered:
Aug. 1 to Oct. 31, 1953

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Institute of Polymer Research
Polytechnic Institute of Brooklyn
99 Livingston Street
Brooklyn 1, New York

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POLYTECHNIC INSTITUTE OF BROOKLYN

PROGRESS REPORT

OFFICE OF NAVAL RESEARCH CONTRACT Nonr-1129(00),
PROJECT NR 036-012.

The program outlined in our research proposal, and as reiterated in our previous reports, was continued. Our work comprised in particular further molecular characterization of polyvinyl butyrals and acetates, including studies by hydrolysis and reacetylation, and adsorption experiments. We also made progress in the phase of our work, recently entered upon, on the oxidation of butyrals by chromic acid.

As for the adsorption, previous work was handicapped by the lack of adequate temperature control. The necessary equipment has now been completed and a new isotherm has been determined. The work is in active progress.

Molecular weights of the three polyvinyl acetates PVAc XYHL, XYSG and of the reacetylated XYHL, were measured by light-scattering, as were those of the polyvinyl butyrals (PVB) made from the XYHL and XYSG acetates. Radii and weight average molecular weights are reported in Table I. Measurements were made at room temperature using methyl ethyl ketone as solvent. The molecular weights are corrected for dissymmetry and depolarization.

T A B L E I

<u>Sample</u>	<u>B x 10⁶</u>	<u>M_W</u>	<u>R(Å)</u>
PVB (XYSG)	.69	800,000	388
PVB (XYHL)	.323	540,000	327
PVAc (XYSG)	4.4	275,000	204
PVAc (XYHL)	4.8	155,000	188
* PVAc (XYHL)	1.6	150,000	367

* after reacetylation

R is the radius of the molecule and is defined by

$$R^2 = \frac{1}{N} \sum_{k=1}^N R_{ok}^2$$

where R_{ok} is the distance from the center of mass of the molecule to the k^{th} polymer segment and N is the number of segments.

B is the second virial coefficient as obtained from the light scattering equation $H C \gamma + RT M^{-1} + 2 BC$.

M is the molecular weight of the polymer, γ turbidity, C, concentration, and H, a constant characteristic of the polymer-solvent system.

The relative values obtained for PVAc XYHL before and after reacetylation are of interest. The molecular weights remain the same, but the radii of the molecules increase greatly. We see further that the second virial coefficient is lower for the reacetylated material than for the original polyvinyl acetate. A sample of reacetylated XYSG is now being prepared, and the data on that material will help in

the analysis of this observation.

However, it was noted that the reacetylated PVAc passed through a sintered glass filter much more slowly than the sample before reacetylation. This indicates the presence of gel or microgel particles. The measurement of molecular size by light-scattering is much more sensitive to small amounts of large size particles than the molecular weight (R is a Z average, M_w a weight average), and a few gel particles might lead to the substantially higher values of R observed. The drop in the second virial coefficient, being indicative of reduced solubility, fits into this picture and may be due to free hydroxyl groups which lead to molecular association.

For the oxidation experiments, the butyral resins were dissolved in 95 % isopropanol to yield a concentration of 0.85 %. To this, an equal volume of a solution of 0.6 ml. of 85 % orthophosphoric acid in 10 cc. of isopropanol was added. As a rough indicator for reactions taking place, viscosities of the mixtures were measured. This was helped by the fact that the components of the mixture had comparable viscosities. No changes in viscosities were observed in 48 hours at room temperature. The same procedure was repeated at 63°C.; again there was no observable change, indicating that phosphoric acid alone has little effect on the butyral resin under these conditions, at least not one that would

influence viscosities.

However, when a solution of 50% CrO₃ in water is added to the resin-phosphoric acid mixture, the solution turns rapidly cloudy, and the viscosity drops immediately. A fine colloidal suspension is obtained at first which in the course of 5 to 10 minutes starts separating as a precipitate. Hence further viscosity readings of the suspension are of little significance.

Precipitate and Filtrate are now further analyzed. Our results to date indicate that the CrO₃ is quickly reduced to Cr³⁺, not necessarily by the butyral but by the alcohol. The Cr³⁺-ions complex heavily with the butyral or polyvinyl alcohol and form a compound which is insoluble in all but strong H-bond breaking solvents. The complex can be split by high or low pH's, but not very well by other chelating agents. The recovered butyral tenaciously holds small amounts of Cr³⁺ and does not seem to be much degraded.